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Intensive Optical Field Improves the Photopolymerization-induced Alignment Quality of Liquid Crystals

Sun Li^a and Wang Shumei^b

^aDepartment of Biochemistry, Yantai University, Yantai, 264005, P. R. China

^bLab Of Excited State Processes, Changchun Institute of Physics, Changchun 130021, P. R. China

E-mail: sunwangl@public.ytpptt.sd.cn

Abstract

Based on a novel concept that intensive optical field may improve alignment of polymer films photopolymerized by linearly polarized laser light, we investigated effects of instantaneous intensity of the laser light and viscosity of the films on alignment of liquid crystals on the photopolymerization-induced anisotropic films. The intensity and the viscosity are the two essential factors related intimately to magnitude and relaxation time of the reorientation Kerr effect. The experiments demonstrated that the increase in the intensity and the decrease of the viscosity improved the photopolymerization-induced orientation of the films. Based on the photochemical points, we discussed causes of the improvement.

Key words: Kerr Effect; Photo-induced Alignment; Photopolymerization; Liquid Crystals

1. Introduction

Recently photo-induced alignment of liquid crystals (LCs) on thin layers of polymers has been attracting many researchers owing to its great potential for replacing the conventional rubbing techniques. The rubbing techniques often causes electric and mechanical damage to the polymer films, such as the generation of static charge, dusts and grooves in the process. The photo-induced LC-aligning techniques extensively reported¹⁻¹¹ are established mainly on the bases of either anisotropic photoisomerization of dichroic dyes doped in polymer films¹⁻⁴ or anisotropic photopolymerization of actinic polymer films⁵⁻¹⁰ under linearly polarized light. For both of the techniques, the orientation quality of the polymer films, on which LCs anisotropically align, depends directly upon the efficiency of the anisotropically induced photoreactions in the path of the acting light, because the orientation originates from the photoreaction products of the actinic molecules in the films whose transition dipolar moments are parallel to the polarization direction of the acting light and from the steric interaction exerted by the products on their adjacent molecules.

Paparo et al¹¹ reported that the optical Kerr effect associated with light-induced molecular orientation largely enhances the alignment of anisotropic molecules in a transparent liquid doped with a small amount of dye. They ascribed the enhancement to two processes: electronic excitation of molecules induced by light absorption that generates oriented populations of excited and ground-state molecules and intermolecular interactions originated from photo-induced molecular transition dipole that generates an anisotropic intermolecular force field; the orienting actions add to the direct optical field action¹¹. In accordance with the concept of reorientational Kerr effect, intensive optical fields of laser pulses can distort electron distribution of a molecule and lead to generating an instantaneous dipolar moment in it. Driven by the optical field, the induced dipolar moment may rotate and strive to be parallel to the field direction. Consequently, structural parts of the molecule related to the range of the distorted electron distribution reaching may reorientate with the induced moment. Under specified conditions, the reorientational Kerr effect is a main contributor of third-order optical nonlinearity, and it can be evaluated by magnitude of third-order refraction. Moreover, the relaxation time of the Kerr effect is intimately related to viscosity coefficient of liquid systems and to excited-state lifetime of molecules when wavelengths of laser pulses are within absorption bands of the molecules.

Here we present an approach of photopolymerization-induced LC orientation based on the concept that the intensive optical field of linearly polarized laser light may enhance the photopolymerized-induced anisotropic alignment of polymer films. A coumarin derivative was used as the actinic prepolymer; in it the coumarin structure, equivalent to dichroic dyes, is the part that responds to the active light field of high intensity and reorientates with the direction of the light field. The reactive bond of (2+2)-cycloaddition lies in the coumarin part, and its excited-state dipolar moment is parallel to polarization of the coumarin structure. This feature favors the anisotropic polymerization induced by the laser light. The obtained results demonstrate that reorientational Kerr effect can improve anisotropic alignment of the polymerized spin-coated polymer films.

2. Material and methods

Actinic prepolymers of spin-coated polymer films are coumarin derivatives (Fig. 1). They can polymerize by (2+2)-cycloaddition under 355nm linearly polarized light⁵. The polymer films were made with the actinic prepolymer spin-coated on ITO glass substrates. The films were used to polymerize immediately after they were made in unsolidified state, or after solidified at 130°C for 2h.

Anisotropic photopolymerization of the spin-coated polymer film, either fresh or solid, was performed for 10min under linearly polarized 355nm laser pulses, third harmonic of Q-switched mode-locked Nd:YAG laser, of 35ns (FWHM) and 250ps (FWHM) pulse train with 7 pico-pulses whose intervals are 7.5ns. Fig.2 shows the set-up for the experiment. Both of the active lights had same energy. Three kinds of the photopolymerized films were used to fabricate LC cells of conventional sandwich type.

Third-order nonlinearity of the used actinic prepolymers was measured by Z-scan technique¹². The prepolymers dissolved in N,N-Dimethylformamide at a weight ratio of $\sim 0.1\%$ was filled in a 1.0mm thick cuvette. The Z-scan was performed with the third harmonic of Q-switched mode-locked Nd:YAG laser in the TEM₀₀ mode. The 250ps (FWHM) pulse train with 7 pico-pulses whose intervals are 7.5ns were focused to a beam radius of 12.3 μ m (HW 1/e² M), and $I_0 = 24.8\text{MW/cm}^2$

3. Results and Discussions

We experimentally investigated effects of two essential factors on photopolymerization-induced orientation of the polymer films in order to study the influence of reorientational Kerr effect, an intensive optical field effect, on photo-induced alignment of liquid crystals. One is intensity of acting light, and the other is viscosity of the polymer films. In evaluating the intensity effect, we anisotropically photopolymerized the solidified polymer films by exposing them respectively to the 355nm 250ps(FWHM) pulse trains and the 355nm 35ns(FWHM) pulses. The single pulse train has the same energy as the single 35ns pulse; however, the ratio of their intensities (I_{ps}/I_{ns}) is 35 for the same irradiation area supposed that average energy per pulse in the pulse train is 0.25E. The intensities are calculated from formula of the peak irradiance $I=E/S\tau$, where E is pulse energy, S is irradiation area and τ is pulse duration. Instead of single picosecond pulses, We used picosecond pulse trains to induce anisotropic photopolymerization of the polymer films to ensure that the films get enough illumination for the photoreaction, which was the reason that the picosecond pulse trains were used in the Z-scan. In investigating the viscosity effect, we substituted the fresh spin-coated polymer films not solidified by baking for the baked films; but they were heated at 70°C meanwhile exposed to the 250ps pulse trains. As shown in Fig.3, (b) presents the LC alignment better than (a), and (c) is the best one. These results exhibit that the increase in the laser intensity and the decrease of the polymer film viscosity improve the reorientation of the photopolymerization-induced films.

The peak-valley configuration obtained from the normalized Z-scan curve (not shown) indicated that the nonlinearity of the prepolymer was negative. Its nonlinear refractive index under these conditions was determined to be $n_2 = 2.37 \times 10^{-9}$ esu. The rise-time of a thermal lens in a liquid is determined by the acoustic transit time $\tau = \omega / v_s$, where v_s is the velocity of sound in the liquid and ω_0 beam waist radius. In the present experiment, $\omega_0 = 12.3 \mu\text{m}$ and $v_s = 10^5 \text{cm/s}$, we obtained a risetime of 12.3 ns. Obviously, owing to accumulating effect at the end of several pulses electrostrictive and thermal effects may produce. Because the picosecond laser pulse trains have only seven pico-pulses and 7.5 ns pulse interval¹³, they are not major origins of the nonlinearity. Therefore, the major origination of the third-order nonlinearity is reorientational Kerr effect. In contrast, the electrostrictive and thermal effects are major origins of the prepolymer nonlinearity under the optical pulse with 35 ns (FWHM) duration. That means the prepolymer molecules can be reorientated when the optical intensity is high enough to result in the Kerr effect.

When the two kinds of acting light have the same energy at 355 nm, the photopolymerization probability of the films is equivalent in the range of linearity. When the intensity of acting light increases higher enough, optical nonlinearities occur. There are several origins of third-order optical nonlinearity in isotropic media, such as thermal effect, electrostriction and reorientational Kerr effect. Of them only the reorientational Kerr effect is anisotropic. Obviously, the reorientational Kerr effect may enhance the anisotropic alignment of the prepolymers in the films; therefore, it gives its contribution to the improvement of the quality of the anisotropic photopolymerization in the films in our experiments.

The reorientational Kerr effect leads to the increase in the number of the pairs of the actinic molecules that couple in spatial positions for the anisotropic photopolymerization, so that the probability of the reaction is increased. Consequently, it improves the anisotropic alignment of the polymer films. In addition, the low viscosity of the unsolidified films may make the Kerr effect come into full play to the anisotropic photopolymerization; and it may be favorable to the steric interaction to enhance the anisotropic reorientation of the films. Furthermore, the gradual evaporation of solvent in the films may contribute to fixing the orientated alignment in them. In the solidified polymer films, only the molecules the angles of whose transition dipolar moments with respect to wave vector directions of acting lights are within the range from 0° to 45° are easily photopolymerized no matter what directions of the acting-light wave vector are with respect to the film plane. Therefore, pretilt angles of the photopolymerization-induced film alignment can not be changed identically with

the wave vector directions of the acting lights changing, unless the polymer molecules may reorientate along with the optical fields before they are photopolymerized. Reorientation Kerr effect may efficiently cause the polymer molecules employed to make spin-coated films to reorientate adequately with the field direction changing¹⁴ if in intensive optical fields, electron distribution distortion of them covers most part of their structures, such as molecules with large conjugated electron systems. Such being the case, pretilt angles of the film alignments may be satisfactorily controlled by adjustment of optical field direction of acting lights.

Probability of anisotropic photo-reactions, on the photochemical points of view, are critically decided by the directional identity of transition dipolar moments of reactive molecules with polarization direction of the acting light and by correct coupling of spacial positions between two reactive polymers. However, the increase in the photo-reactions which the actinic polymers whose transition dipolar moments are somewhat unparallel to the polarization direction of the acting light participate in may decrease the established anisotropy of the polymer films^{6,9}. Therefore the number of molecules contributing to generating high qualitative anisotropy of the polymer films are pretty limited because all the molecules of the films are isotropically distributed. Furthermore, the anisotropic reorientation originated from the steric interaction between the photochemical products and their adjacent molecules, as well as that of the prepolymers, is also pretty restricted by the viscosity of the films in solid state^{3,5,8}. Therefore, either increasing the efficiency of the anisotropic photo-reactions or decreasing the viscosity restriction of polymer films may improve the reorientational quality of the films and that of the adjacent LC molecules.

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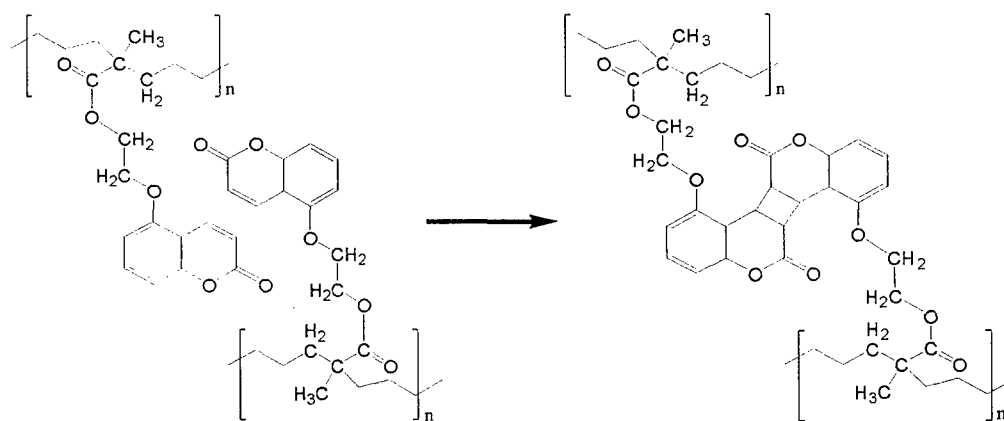


Fig.1 The structure of two actinic repolymers (left) and their dimerization (right) by intermolecular photo-induced (2+2) cycloaddition

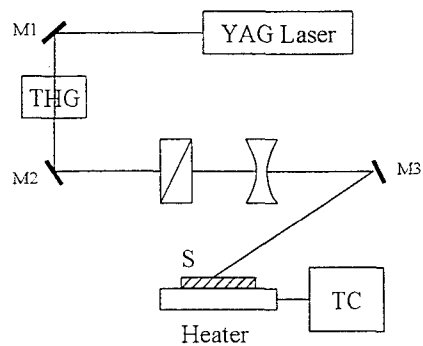
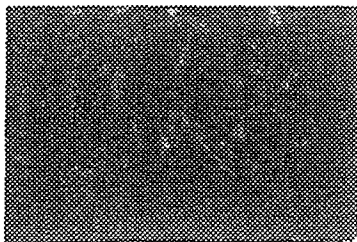
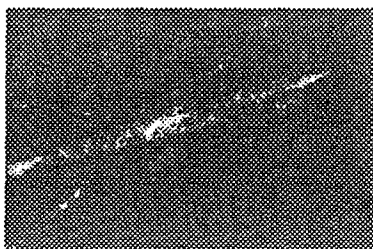


Fig.2 A new experimental setup used for unsolidified polymer films to be photopolymerized under illumination of linearly polarized laser light. S, sample; TC, temperature controller.

A



B



C

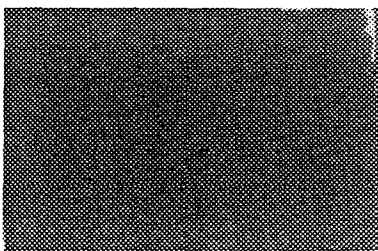


Fig.3 Polarized microscopic photographs of the LC cells fabricated with three differently photopolymerized polymer films: (a) the baked films photopolymerized by exposition to 355nm 35ns laser pulses; (b) the baked films by exposition to 355nm 250ps pulse trains; (c) the unsolidified films by exposition to 355nm 250ps pulse trains.